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KINETIC STUDIES OF ATOM TRANSFER RADICAL
POLYMERIZATION OF METHYL ACRYLATE

by

H. Paik, K. Matyjaszewski

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Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

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Kinetic Studies of Atom Transfer Radical Polymerization of Methyl Acrylate

Hyun-joong Paik and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh, PA 15213

Introduction

The perfect control over polymerization, including chain architecture, end groups, molecular weight and its distribution, is one of the most important goals for synthetic polymer chemists. This control can broaden the realm to new materials without using new monomers.¹ After Szwarc first reported living polymerizations,^{2,3} e.g. polymerization in which chain termination and chain transfer are absent, it has been regarded as the most promising method for control.

In radical polymerization, it is impossible to achieve a truly living process due to bimolecular termination reactions such as coupling and disproportionation which are absent in ionic polymerization. Therefore, instead of a living process in true meaning, approaches to the controlled or "living" polymerization in which chain breaking reactions exist, but in tolerable and controllable proportions, have been proposed by various means.⁴ Radical polymerization has many advantages over ionic polymerization, such as a large variety of polymerizable and copolymerizable monomers and less stringent reaction conditions compared to ionic polymerization.

Atom Transfer Radical Polymerization (ATRP), whose concept came from Atom Transfer Radical Addition,^{5,6} was recently reported as a route to the synthesis of well defined polymers of such monomers as styrene, acrylates and methyl methacrylates.^{7,8}

In this report, the kinetic studies of the polymerization of methyl acrylate with a homogeneous and heterogeneous catalytic system will be described. Also, the evolution of molecular weights and polydispersities with conversion will be discussed.

Experimental Materials

Methyl acrylate [MA] was stirred over CaH₂ overnight and distilled under vacuum before polymerization. Methyl 2-bromopropionate [MBP] was used as received from Aldrich without purification. 4,4'-Di-*tert*-butyl-2,2'-bipyridine [dTbipy] was prepared according to the known procedure⁹ and 4,4'-di-(5-nonyl)-2,2'-bipyridine [dNbipy] was obtained from Reilly Industries. CuBr was purified according to the literature.¹⁰ CuBr₂ was used without further purification.

Polymerization

The general procedure for the polymerization was as follows: to a glass tube, CuBr, ligand, initiator and monomer were added. The solution was degassed two times by the "freeze-pump-thaw" method and sealed under vacuum. The tube was placed in an oil bath thermostatted at desired temperature. At timed schedule, the tube was removed from the oil bath and opened. The mixture was dissolved in a known amount of THF and analyzed.

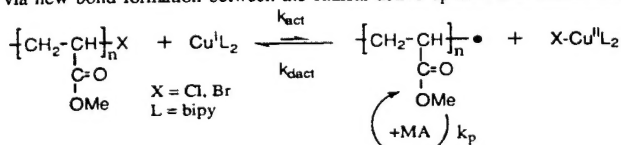
Characterization

The monomer conversion was determined by Gas Chromatography using a Shimadzu GC-14A with DB-WAX column. Molecular weights and polydispersities were measured using Phenogel GPC columns (guard, linear, 1000 Å and 100 Å) and 410 refractive index detector. Narrow polystyrene standards were used to calibrate the columns.

Results and Discussion

General Features

The key point in controlled radical polymerization is the establishment of a rapid equilibrium between dormant and active species. The equilibrium should lie towards the dormant species to lower the stationary concentration of active species, thus minimizing the termination reactions. In ATRP, this is accomplished by cleavage and formation of halogen-carbon bond by copper / bipy complex. The propagation proceeds via new bond formation between the radical active species and monomer.



Mechanistic Studies

According to the proposed mechanism, the rate of propagation can be described by the following equations.

$$R_p = k_p^* [M] [P^*] = k_p^* K_e [M] [P-X] \frac{[\text{Cu}^{\text{I}}\text{L}_2]}{[\text{X-Cu}^{\text{II}}\text{L}_2]} = k_p^{\text{app}} [M] \quad \text{eq. 1}$$

$$K_e = \frac{k_{\text{act}}}{k_{\text{dact}}} = \frac{[P^*][\text{X-Cu}^{\text{II}}\text{L}_2]}{[\text{Cu}^{\text{I}}\text{L}_2][P-X]} \quad \text{eq. 2}$$

$$k_p^{\text{app}} = k_p^* [P^*] = - \frac{d \ln [M]}{dt} \quad \text{eq. 3}$$

In order to support the proposed mechanism of propagation, basic kinetic studies were performed. The internal order in monomer and external order in initiator, copper(I) complex and copper(II) complex.

To satisfy the requirement¹¹ for controlled radical polymerization, e.g. fast initiation comparable to propagation, methyl 2-bromopropionate, which has a very similar structure to the end group of dormant polymer, was used. A complex of CuBr / dTbipy or dNbipy (1:2 mole ratio) was used as the catalyst. The reaction mixture was not completely homogeneous with the copper(I) / dTbipy complex, but it was homogeneous with dNbipy. The first order kinetic plot was linear which indicated that the number of active species was constant during the polymerization. (Fig 1) The rate has first order dependence on the initiator concentration (slope = 0.89). (Fig 2)

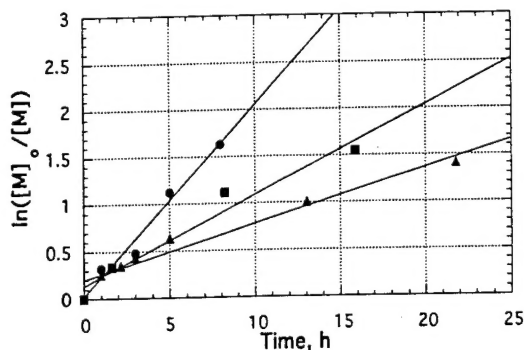


Figure 1. Effects of various concentration of initiator on polymerization kinetics, [MA]₀ = 11.2 M; [MBP]₀ = 0.112 M (●), 0.056 M (■), 0.028 M (▲); [CuBr]₀ = 0.056 M; [dTbipy]₀ = 0.112 M; Temp = 90 °C

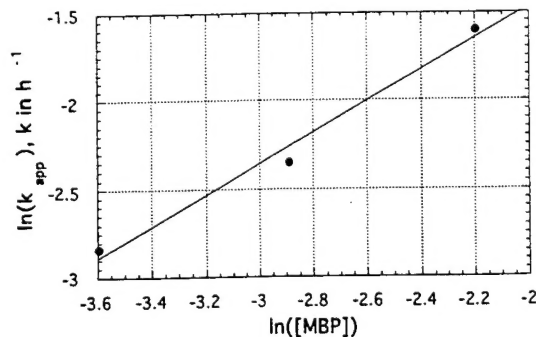


Figure 2. Dependence of apparent rate coefficient (k_{app}) on the initiator concentration in the polymerization of MA, [MA]₀ = 11.2 M; [CuBr]₀ = 0.056 M; [dTbipy]₀ = 0.112 M; Temp = 90 °C

The linear increase of molecular weights versus conversion was observed with good correlation to predicted values, $DP = \Delta[M]/[I]_0$ and the molecular weight distribution was narrow, $M_w/M_n = 1.2$. These results indicate that the chain breaking processes could be neglected leading to a controlled polymerization. (Fig 3).

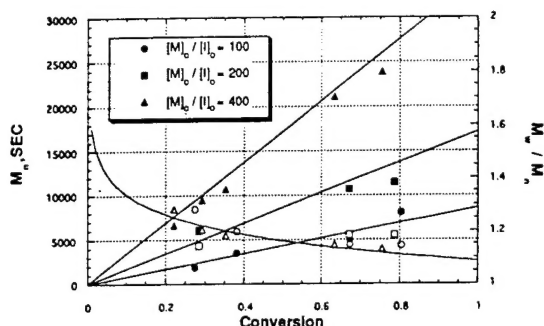


Figure 3. M_n and M_w/M_n dependence on conversion for different $[monomer]_0/[initiator]_0$ ratios for bulk ATRP of methyl acrylate $[MA]_0 = 11.2$ M; $[MBP]_0 = 0.112$ M; (●, ○), 0.056 M (■, □), 0.028 M (▲, △); $[CuBr]_0 = 0.056$ M; $[dTbipy]_0 = 0.112$ M; Temp = 90 °C

Figure 4 shows that the dependence of the rate constant on the initial catalyst concentration is first order for the homogeneous catalyst system (copper(I) / dNbipy). The changes in concentration of non-homogeneous catalyst system (copper(I) / dTbipy) showed little effect on the propagation rate, presumably due to the solubility limit. The slightly negative slope ordered for dTbipy may be due to additional solubility limitations of the deactivator Cu(II). (vide infra)

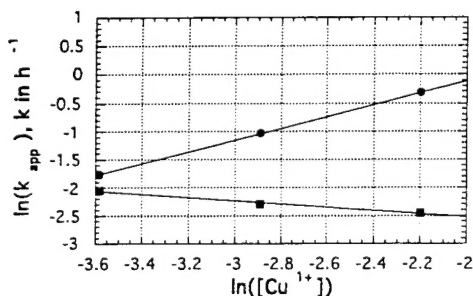


Figure 4. Effects of various concentrations of catalyst on polymerization rate $[MA]_0 = 11.2$ M; $[MBN]_0 = 0.056$ M with CuBr / dNbipy (1:2, ●) and CuBr / dTbipy (1:2, ■); Temp = 90 °C

As expected, the apparent rate constant for copper(I) / dNbipy system had inverse first order on the concentration of copper(II) bromide. (Fig 5) The slope of the $\ln(k_{app})$ versus $\ln(1/[Cu^{2+}])$ for copper(I) / dTbipy system (0.43) means that the propagation rate is less affected by the concentration of copper(II)bromide in non-homogeneous system.

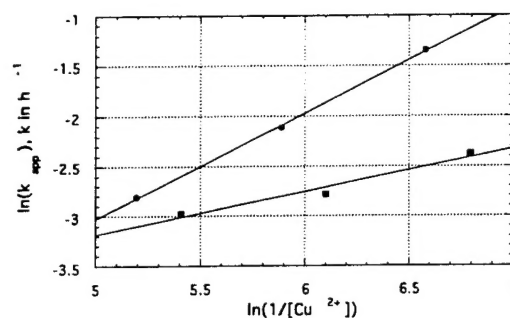


Figure 5. Effects of various concentration of copper(II) bromide on polymerization rate with CuBr₂; $[MA]_0 = 11.2$ M; $[MBN]_0 = 0.056$ M; $[CuBr]_0 = 0.056$ M; $[dNbipy]_0 = 0.112$ M (●), $[dTbipy]_0 = 0.112$ M (■); Temp = 90 °C

Synthesis of High Molecular Weight Polymer.

The synthesis of polymers with molecular weights up to 10^5 was attempted. The experimental molecular weight had good correlation with the theoretical values up to $M_n = 80,000$ and molecular weight distribution was narrow ($M_w/M_n = 1.2$). (Fig 6)

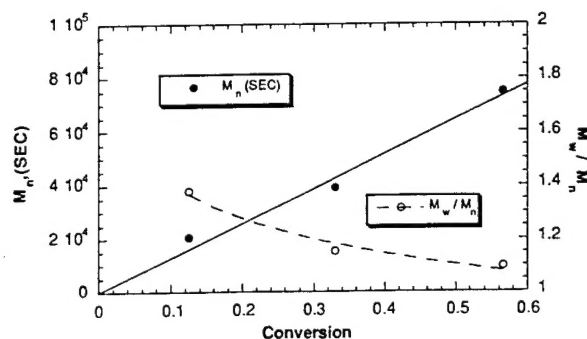


Figure 6. M_n and M_w/M_n dependence on conversion for ATRP of methyl acrylate $[MA]_0 = 11.2$ M; $[MBP]_0 = 0.0074$ M ($[M]_0/[I]_0 = 1500$); $[CuBr]_0 = 0.0074$ M; $[dTbipy]_0 = 0.0148$ M

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